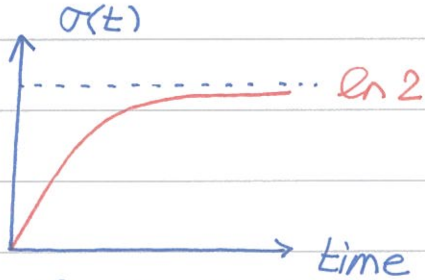
HH0106 Thermal and Information Entropies

In previous lectures, we learned two types of entropies: information entropy σ and thermal S.

$$\boxed{\sigma = \sum_s -P_s \ln P_s}$$

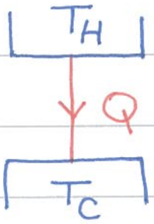


In the simple version of the dog-flea model, we see how $\sigma(t)$ increases monotonically with time (up to statistical fluctuations). It seems to follow the second law.

On the other hand, we can also define the thermal entropy from the ratio of heat and temperature,

$$\boxed{\Delta S = S(B) - S(A) = \int_A^B \frac{dQ}{T}}$$

use $dQ = TdS$ for reverisible processes



$$\Delta S = -\frac{Q}{T_H} + \frac{Q}{T_C} > 0$$

We learned different forms of the second law are equivalent to the common sense: Heat flows from T_H to T_C!

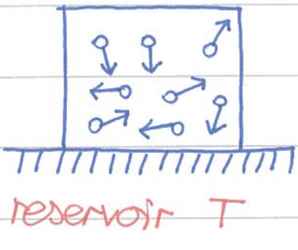
In the notes here, we would like to establish the relation between information entropy σ and thermal entropy S.

$$\boxed{S = k\sigma}$$

k is the Boltzmann Constant

Yes, they are simply proportional to each other.

① Boltzmann distribution in thermal equilibrium. Suppose a system is in thermal contact with a reservoir of temperature T. Because they can exchange energy, the energy of the system is not definite. Instead, it is described by a probability distribution.



That probability distribution in thermal equilibrium turns out to be the Boltzmann distribution,

$$\boxed{P(E_s) \propto e^{-E_s/kT}} \leftarrow$$

It is more likely to find lower energy states

Let us apply the Boltzmann distribution to derive the Maxwell distribution of molecular speed in the ideal gas.

For an ideal gas, we would like to know the probability fn,

$$P(\underset{\text{where}}{\vec{r}}, \underset{\text{how fast}}{\vec{p}}) \propto e^{-p^2/2mkT} \leftarrow E_s = \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2). \text{ total energy.}$$

It is quite interesting that the notion of phase space $(x, y, z; p_x, p_y, p_z)$ becomes very helpful. Write down the proportional constant explicitley,

$$\boxed{P(\vec{r}, \vec{p}) = \frac{1}{Z} e^{-p^2/2mkT}}$$

We can find out the const Z by probability conservation.

Ⓐ $\sum_{\vec{r}} \equiv \int dx \int dy \int dz$ and $\sum_{\vec{p}} \equiv \int dp_x \int dp_y \int dp_z$

Ⓑ integral formula $\int_{-\infty}^{+\infty} dp_x\, e^{-p_x^2/2mkT} = (2\pi mkT)^{\frac{1}{2}}$.

$$\sum_{\vec{r}} \sum_{\vec{p}} P(\vec{r}, \vec{p}) = 1 \longrightarrow \frac{1}{Z} \sum_{\vec{r}} \sum_{\vec{p}} e^{-p^2/2mkT} = 1$$

Thus, $Z = \sum_{\vec{r}} \sum_{\vec{p}} e^{-\frac{1}{2mkT}(p_x^2 + p_y^2 + p_z^2)} = V\left(\sqrt{2\pi mkT}\right)^3$.

$$\longrightarrow \boxed{Z = V \cdot (2\pi mkT)^{\frac{3}{2}}}$$

This important constant is called "partition function".

Note that the partition function $Z \propto VT^{\frac{3}{2}}$ will lead to $\sigma = \sigma(V, T)$ as shown below.

According to the definition of Shannon entropy,

$$\sigma = \langle -\ln P \rangle = \left\langle \ln Z + \frac{p^2}{2mkT} \right\rangle$$

$$\rightarrow \sigma = \ln Z + \frac{1}{kT}\left\langle \frac{p^2}{2m} \right\rangle = \underline{\ln Z + \frac{3}{2}}$$

Write down the V and T dependence explicitly,

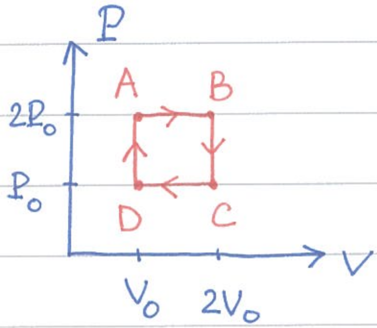
$$\boxed{\sigma = \ln V + \frac{3}{2}\ln T + \sigma_0} \rightarrow$$

σ_0 is some const. We obtain the information entropy for a single particle.

Because an ideal gas consists of N independent particles,

$$\boxed{\sigma_N = N\sigma = N\ln V + \frac{3}{2}N\ln T + \text{const}}$$

Let us go back to the previous example of a square loop.



Note that $\underline{T_B = 2T_A = 2T_C = 4T_D}$.

$$\sigma_N(B) - \sigma_N(A) = N\ln(V_B/V_A) + \frac{3}{2}N\ln(T_B/T_A)$$

$$= \underline{\frac{5}{2}N\ln 2}$$

Compare it with the thermal entropy,

$$S_N(B) - S_N(A) = nC_p\ln 2 = \underline{\frac{5}{2}Nk\ln 2} \rightarrow \boxed{S_N = k\sigma_N}$$

One can try to compute $\Delta\sigma_N$ and ΔS_N for other processes and verify the simple relation always holds ☺

Finally, let's derive the Maxwell distribution for molecular speed. Consider the average of some quantity $Q = Q(v)$ that only depends on the speed. (not velocity!)

only depends on v!

$$\underline{\langle Q(v) \rangle = \sum_{\vec{r}} \sum_{\vec{p}} \left(\frac{1}{Z} e^{-p^2/2mkT} \right) \cdot Q(v)}$$

Carry out the integral over position $\vec{r}$,

$$\langle Q(v)\rangle = V\cdot\frac{1}{Z}\int dv_x\int dv_y\int dv_z\; m^3\cdot e^{-\frac{mv^2}{2kT}}\,Q(v)$$

$$= \int dv_x\int dv_y\int dv_z\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}}\,Q(v)$$

The integral over velocity can be turned into the integral over speed

$$\int dv_x\int dv_y\int dv_z\,(\cdots) = \int_0^\infty dv\;4\pi v^2(\cdots)$$

Thus, the average of $Q=Q(v)$ simplifies into 1D integral,

$$\langle Q(v)\rangle = \int_0^\infty dv\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2 e^{-\frac{mv^2}{2kT}}\times Q(v)$$

Because the above equation is valid for arbitrary function $Q(v)$, we come to the conclusion that

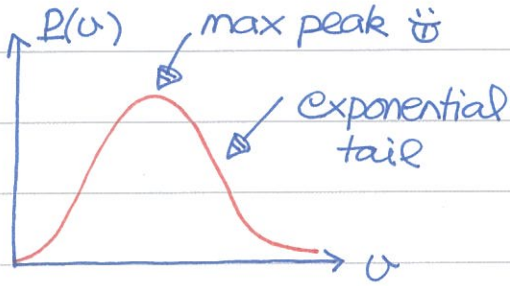
$$\boxed{P(v) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} 4\pi v^2\, e^{-mv^2/2kT}}$$

Maxwell distribution for molecular speed.

speed

degeneracy

Boltzmann factor.



Because of the degeneracy factor $4\pi v^2$ in 3D, the probability function exhibits a maximum peak and the slow-speed regime is suppressed.

⑪ Heat and entropy in reversible processes. According to the definition of thermal entropy by reversible processes,

$$\Delta S = S(B)-S(A) = \int_A^B \frac{dQ}{T} \longrightarrow \boxed{dQ = TdS}$$

In the following, I would like to show that

$kTd\sigma = dQ$, that is to say, $\boxed{S = k\sigma}$ in general.

The internal energy of a statistical system is

$$U = \sum_s P_s E_s \longrightarrow \boxed{dU = \sum_s P_s dE_s + E_s dP_s}$$

Let us focus on the first term,

$$\underbrace{\sum_s P_s dE_s} = \sum_s P_s \vec{\nabla} E_s \cdot d\vec{r} = \underbrace{-\left(\sum_s P_s \vec{F}_s\right) \cdot d\vec{r}}$$

In above, we have used the relations, $dE_s = \vec{\nabla} E_s \cdot d\vec{r}$ and the conservative force $\vec{F}_s = -\vec{\nabla} E_s$.

Thus, $\boxed{\sum_s P_s dE_s = -\langle \vec{F} \rangle \cdot d\vec{r} = -pdV = -dW\,!}$

Now we turn to the second term and try to find the relation with the information entropy.

$$d\sigma = d\left(-\sum_s P_s \ln P_s\right) = \sum_s -\ln P_s dP_s - \cancel{P_s}\frac{1}{\cancel{P_s}} dP_s$$

$P_s = \frac{1}{Z} e^{-E_s/kT}$ Boltzmann dist.

$$= \sum_s (\ln Z - 1) dP_s + \sum_s \frac{E_s}{kT} dP_s$$

$$\longrightarrow \quad d\sigma = (\ln Z - 1) \sum_s \cancelto{0}{dP_s} + \frac{1}{kT} \sum_s E_s dP_s$$

The term $\sum_s dP_s = 0$ because of $\sum_s P_s = 1 = \text{const}$. Thus,

$\boxed{\sum_s E_s dP_s = kT d\sigma}$ Thus, $\boxed{dU = kT d\sigma - dW}$

Compare with the 1st law : $dU = dQ - dW$. It is easy to see that $dQ = kT d\sigma \longrightarrow \boxed{S = k\sigma}$ again!

not just for ideal gas, it is general

Happy

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